

Electronic Supporting Information

**Facile assembly of an efficient CoO_x water oxidation electrocatalyst from
Co-containing polyoxotitanate nanocages**

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Experimental Section

General considerations and Characterizations. Starting materials for the synthetic part of the work were purchased from commercial suppliers and used as received, unless otherwise noted. All chemicals used for the analytical part were of the highest available purity. F-doped tin oxide (FTO) coated glass (sheet resistance 7 ohm sq⁻¹, TEC Glass™ 7) was kindly provided from Pilkington Group Limited, UK. The surface morphologies of the as-prepared TiCo cage modified FTO electrodes (FTO|1 and FTO|2) and the electrodes after electrochemical treatment at 1.35 V vs. NHE (FTO|1* and FTO|2*) were characterized using a JEOL 5800 scanning electron microscope (SEM). The elemental analysis of the films was made using an x-sight light element energy dispersive X-ray (EDX) spectrometer (JEOL 5800). The X-ray diffraction (XRD) analyses of the FTO|1 and the FTO|2 electrodes were carried out using an X'Pert PRO X-ray diffractometer (PANalytical B.V., The Netherland). All electrochemical experiments were performed with an IviumStat CompatStat and carried out as described in the main text. All the potentials were converted to the normal hydrogen electrode (NHE) by adding + 0.197 V.¹

Oxygen detection. O₂ was detected and quantified in an air-tight electrochemical cell using an Ocean Optics fluorescence oxygen probe (FOXY-R). The oxygen probe was inserted into the cell through a tightly sealed rubber septum with continuous O₂ readings at 1 s intervals throughout the experiment (Figure S3): first h without applied potential (control experiment), followed by 1 h water oxidation with an applied potential (1.35 V vs. NHE) and another h without applying potential (control experiment). The total amount of O₂ evolved was calculated from the the amount of O₂ measured in the headspace using the ideal gas law and was corrected for the O₂ in solution using Henry's Law.

Cyclic voltammetry of nanocage 2 in solution. Electrochemical characterization of the novel nanocage **2** (2 mM) was carried out in dichloromethane containing [N(*n*-Bu₄)]BF₄ (0.1 M) as electrolyte (Figure S2). Electrochemical analysis was performed with an Ivium CompactStat potentiostat with a thermostated (25 °C) three-electrode cell. We used a glassy carbon (i.d. = 3 mm) working electrode, a platinum wire counter and a Ag/AgNO₃ (in MeCN) reference electrode. The potentials were measured as the ferrocene/ferrocenium couple with ferrocene as an internal standard, and converted to NHE by adding 0.63 V.²

References

1. D. J. G. Ives and G. J. Janz, Reference electrodes, theory and practice., Academic Press, New York, 1961.
2. L. Duan, Y. H. Xu, M. Gorlov, L. P. Tong, S. Andersson and L. C. Sun, *Chem.-Eur. J.*, 2010, **16**, 4659-4668.

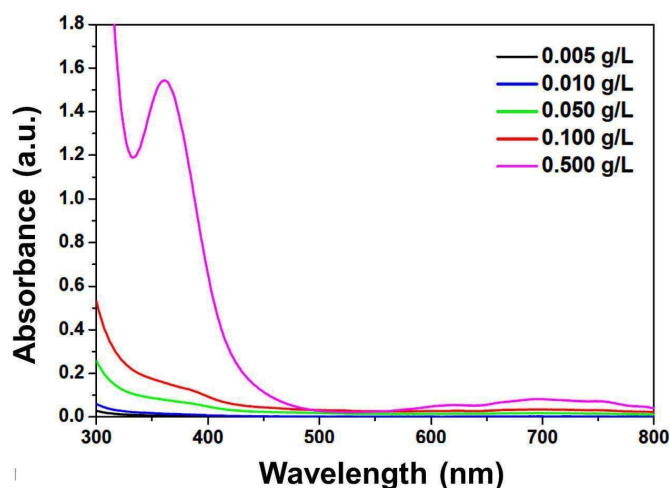


Figure S1. UV-visible spectra of **2**, with various concentrations ranging from 0.005 to 0.5 M, in dichloromethane. The direct (allowed) band gap and indirect (forbidden) band gap for **2** (4.68 ± 0.12 and 3.35 ± 0.05 eV respectively) are similar to those found for **1** (4.64 ± 0.01 and 3.24 ± 0.01 eV, respectively).

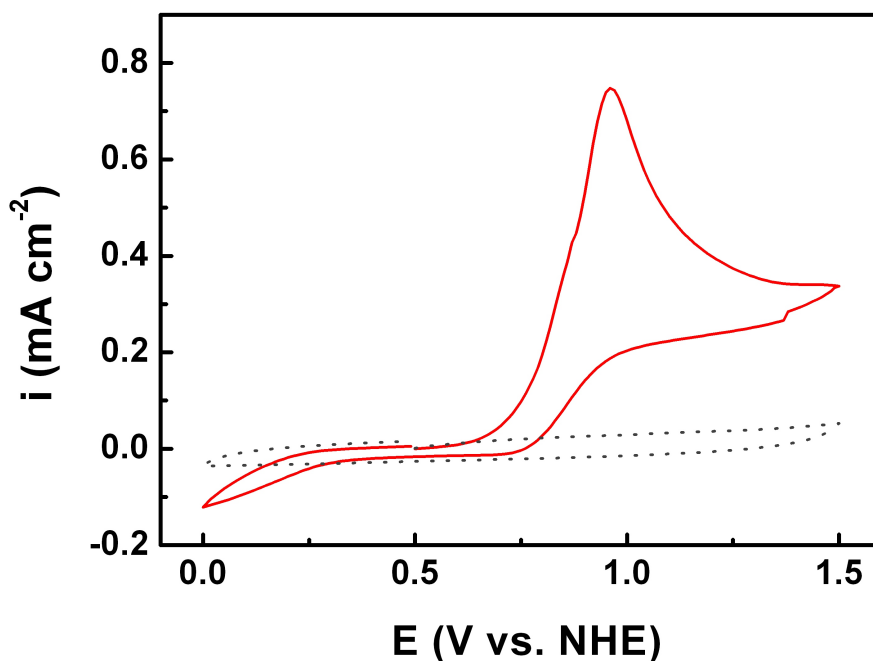


Figure S2. Cyclic voltammograms of **2** (red trace) and a control experiment without **2** (grey dotted trace). The CV of **2** displays one irreversible oxidation wave at $^aE_p = 1.0$ V vs. NHE.

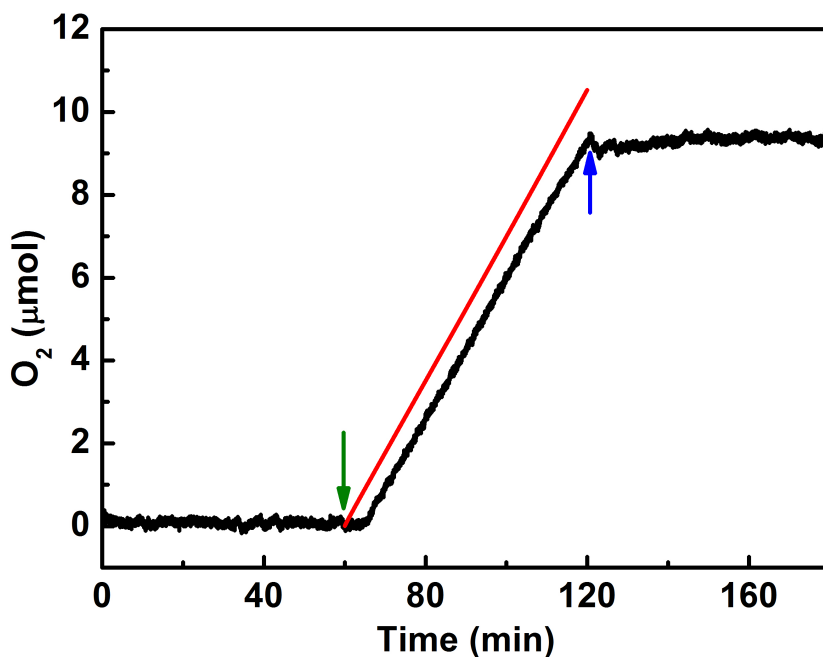


Figure S3. O₂ evolution during controlled potential electrolysis (0.1 M potassium phosphate buffer at pH 7 and 25 °C) with an FTO|1 working, a Pt counter and a Ag/AgCl reference electrode. A potential of 1.35 V vs. NHE was only applied between 60 and 120 min (green and red arrows indicate the beginning and the end of controlled-potential electrolysis, respectively). The amount of O₂ was quantified by an O₂ fluorescence probe (black trace) and the theoretical amount of O₂ with 100 % Faradaic efficiency is shown as a red trace.

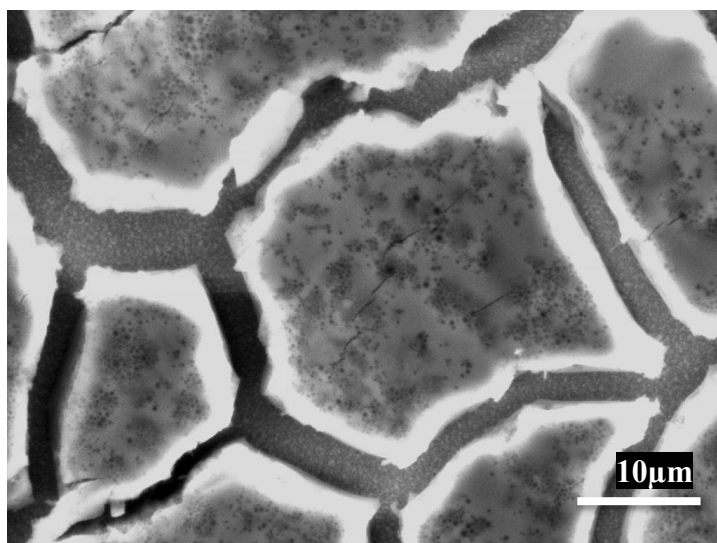


Figure S4. Top-view SEM image of FTO|2* (after electrochemical measurements).

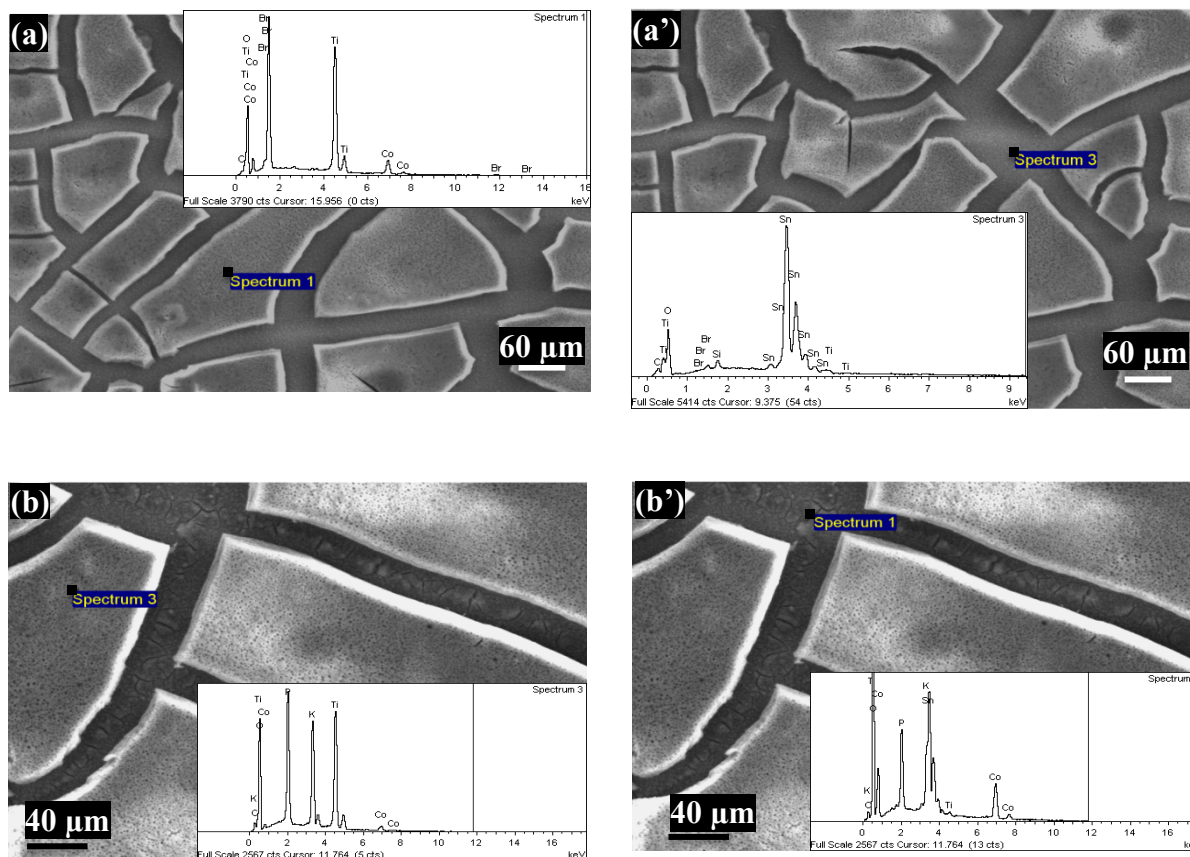


Figure S5. Top-view SEM images of (a-a') the FTO|1 electrode and (b-b') the FTO|1* electrode. EDX data, collected from island area ((a)&(b)) and crack area ((a')&(b')), are shown in the insets.

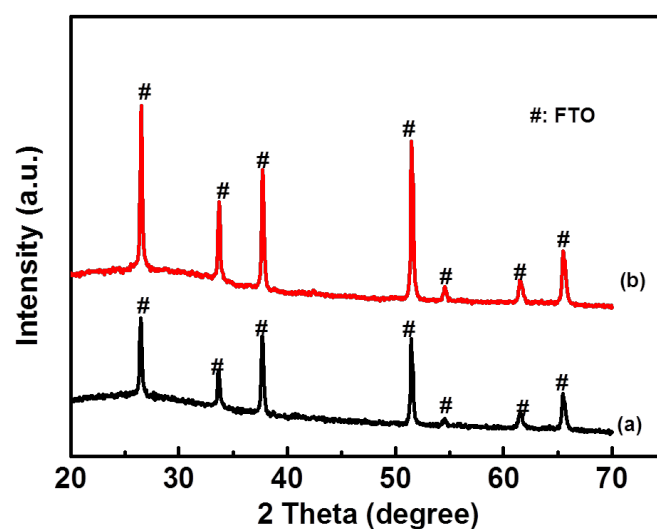


Figure S6. XRD patterns of (a) the as-prepared FTO|1 and (b) the FTO|1*.

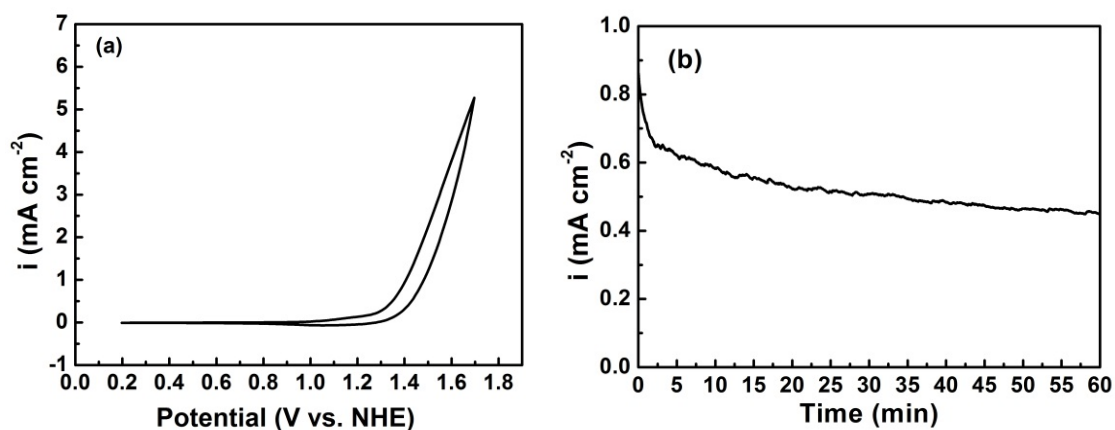


Figure. S7 (a) Cyclic voltammogram of the annealed FTO|1 electrode in potassium phosphate buffer solution (0.1 M, pH 7) at a scan rate of 50 mV s⁻¹. (b) i - t curve of the annealed FTO|1 at 1.35 V vs. NHE in potassium phosphate buffer solution (0.1 M, pH 7).